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TOUGHENING OF THERMOSETTING POLYIMIDES

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by

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August 1979

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DEPARTMENT
OF
MATERIALS SCIENCE
AND
ENGINEERING

SCHOOL OF ENGINEERING
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

RESEARCH REPORT R79-1

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

Toughening of Thermosetting Polyimides

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ABSTRACT

Work directed toward increasing the resistance to crack propagation of thermoset polyimides is described. Unmodified Kerimid 601 has a fracture surface work value of 0.20 in-lbs/in². Dispersed particles of ATBN (amine terminated butadiene acrylonitrile liquid rubber) or of silicone rubber do not raise this value much. By contrast, 5% of well fibrillated Teflon produces an eight-fold increase in fracture toughness. Further process improvements should increase this factor to 20-30.

I. INTRODUCTION

Polyimides are aromatic heterocyclic polymers with good thermal resistance: they maintain useful mechanical properties up to 600°F and function as structural components for land and sea vehicles, aircraft and missiles. Other attractive attributes are their excellent resistance to a wide variety of solvents and the ability to withstand high dosages of radiation. An example of the latter is the absence of any apparent alteration in Kerimid 601 when exposed to 10^{10} rads in a Siloe nuclear reactor (1).

Polyimides are used in the form of adhesives, molded parts, and fiber reinforced composites. Glass (1), graphite (2,3), and other high strength fibers increase the mechanical properties by more than an order of magnitude over those of the bulk resin (1,4).

A polyimide can be either thermoplastic or thermosetting. The thermoplastic forms soften in the vicinity of 300°C, while the thermosetting ones degrade before softening. The latter have extremely low fracture toughness, with Izod impact strengths on the order of 0.3 ft-lb/in. (4). This brittle behavior represents a deficiency which the current research hopes to correct.

There are two categories of thermosetting polyimide prepolymers (3). The first, a condensation type, is prepared by the reaction of an aromatic diamine with aromatic dianhydride or diacid ester (Figure 1). The resulting prepolymer, a polyamic acid or ester, is cured to a polyimide by a condensation reaction known as imidization. If the R associated with the diamine is aromatic, the final product is both infusible and insoluble (5). The second

kind of prepolymer is an addition type. This is a low molecular weight polyamic acid containing reactive aliphatic groups, and it is converted to a low molecular weight polyimide upon imidization (Figure 2). Subsequent pyrolysis of the chain ends yields active species which undergo addition polymerization to produce a cross-linked polyimide.

The chemistry outlined above will be helpful when considering rubber modification to increase fracture toughness. Teflon microfiber impregnation is the other toughening technique explored in this investigation. These methods operate quite differently. Teflon microfibers were invented by Busse and Bowers in 1961 (6). They found that the mastication or milling of unsintered particles of Teflon in molten polyethylene improved melt properties in the fabrication of polyethylene parts. Further examination showed that the Teflon was in the form of finely divided microfibrous and submicrofibrous particles having diameters ranging from 100 Angstroms to a few microns. In later investigations, Schmitt et al. (7) and Landi (8,9) observed more than a tenfold increase in Izod impact strength when PMMA was modified with Teflon microfibers.

The reinforcement of thermosetting resins such as epoxies and phenolics by Teflon microfibers was first achieved by McGarry and Laible (10,11). They reported an order of magnitude increase in toughness, using the double cantilever beam test, was obtained by adding 5% by weight Teflon microfibers to EPON 828 and ERLA 4617. Another significant contribution was their proposed mechanism for microfiber toughening. Although polymeric resins wet Teflon poorly, the extremely high surface area or aspect ratio of the microfibers ensures adhesion. This, plus the ability of the micro-

fibers to undergo large strains, hinders crack growth, because the energy which would be available for crack propagation is absorbed by the drawing of microfibers. Since the toughening effect derives from the Teflon, such highly brittle polymers as the polyimides should respond in the same way.

The second toughening technique studied is rubber modification; some examples are high impact polystyrene (HIPS) and Hycar rubber modified epoxies (12-16). In both, the toughening effect is obtained by the presence of a second phase rubber particle which induces crazing, shear banding, and cavitation. These mechanisms absorb energy otherwise devoted to the initiation and propagation of cracks, thus providing a significant increase in the fracture surface work.

Since polyimides are used at elevated temperatures, the rubbery phase also must have good high temperature resistance. Some ways to meet this requirement are to use an elastomer such as silicone rubber or ones which would react with and be stabilized by the polyimide.

The polyimides studied are laminating resins, normally combined with reinforcing fibers. The toughening methods described, however, would be masked by such fibers. Thus, to evaluate a potential toughening phenomenon, the polyimide was molded without any fibers and tested using the double cantilever beam technique.

II. MATERIALS

A. Kerimid 601

Kerimid 601 is produced by Rhone-Poulenc, and is distributed by Rhodia, Inc. This addition type prepolymer is a fine yellow powder consisting of a mixture of a bismaleimide and an aromatic diamine, at a selected ratio so optimum physical properties can be obtained (17). Curing consists of two reactions, Figure 3, and the presence of the imide group in the prepolymer eliminates the generation of volatiles.

B. LARC 160

LARC 160, an addition polyimide, is produced by NASA Langley (18). The resin is prepared from diethylester of benzophenone tetracarboxylic acid (BTDE), the ethyl ester of norbornene dicarboxylic acid (NE), Jeffamine AP-22, and ethanol, Figure 4. The resulting varnish contains a few percent by weight ethanol, used only as a reaction medium, thus the system is virtually solvent-free. As a laminating resin, this feature promises a distinct advantage over other polyimide resins which may contain as much as 50% solvents by weight.

C. Teflon

The Teflon used for the formation of microfibers is Du Pont TFE Fluorocarbon Resin Powder No. 6 composed of unsintered granules. Sintered granules have a crystallinity content of 20-80%, while unsintered granules exhibit 90-95% crystallinity. Microfibers consisting of the latter type are capable of a large reduction in area when drawn mechanically.

D. Hycar ATBN

Amine terminated butadiene acrylonitrile (ATBN) polymers are liquid elastomers produced by B.F. Goodrich. These contain reactive secondary amine groups, and have been used with aromatic amines in elevated-temperature-curing epoxy systems, producing increased toughness (19). Specifications for the particular ATBN used in this investigation are in Table 1.

E. Silicone Elastomers

The only silicone rubber used in this study was Silastic 450U, produced by Dow Corning. The rubber was vulcanized using 1.5 pph Cadox TS-50, giving a material with an excellent long term retention of mechanical properties at 500°F (20).

III. SAMPLE PREPARATION

A. Kerimid 601

1. Teflon Modification

Table 2 gives a general outline of the various treatments to which the Teflon was subjected, before being incorporated into the Kerimid 601.

2. Silicone Rubber Modification

Silastic 4508 rubber, obtained as a 3/16" thick slab, was cut into 1" wide strips, which were immersed in liquid nitrogen. A frozen strip was then placed against a belt grinder, and the resulting rubber residue was collected.

A belt with well bonded abrasive was used to maintain the purity of the residue. Micrographs show the resulting silicone rubber particles are irregularly shaped and range from a few microns to seventy microns in size, Figure 5.

A single speed 20,000 rpm Waring blender was used to combine the Teflon fibrils or silicone rubber particles with the Kerimid 601 powder. Mixing was facilitated by using isopropyl alcohol as a dispersion medium. The slurry was filtered to remove the alcohol and then dried in 40°C vacuum oven for 18 hours. This produced a good molding powder.

3. ATBN Modification

The viscous nature of the liquid ATBN required manual stirring of the liquid into the powder, producing a heterogeneous molding compound.

All of the compounds were formed into specimens by compression molding, followed by a postcure. The compound was poured into a cold steel mold and compressed at 600 psi. The preform was placed in a second mold preheated to 500°F, and immediately put into the press whose platens had been heated to 500°F. A pressure of 5000 psi was applied. The mold was kept in the press for 20 minutes, after which the specimen was removed and postcured at 250°C for 24 hours, producing a black or dark brown specimen with dimensions 1.56" x 10.06" x 0.2".

4. Machining

Each specimen was machined to 1.2" width and two 1/8" diameter holes were drilled at one end. These were drilled carefully, since the specimen was brittle. Then the specimen was slotted along its entire length on both sides. The resulting double cantilever beam (DCB) specimen is illustrated in Figure 6.

5. Testing

Pins were placed through the holes and the specimen was broken along the web at a constant crosshead rate of 0.1" per minute in the Instron. The area under the load displacement curve, and the crack dimensions were used to obtain a fracture surface work value γ for the specimen by the following equation:

$$\gamma = \frac{A \times F \times \frac{CRS}{CHS}}{200 \times l_c \times w_c}$$

$$\gamma = \text{fracture surface work } \left(\frac{\text{in-lb}}{\text{in}^2} \right)$$

A = area under force displacement curve

F = full scale load (lb)

CRS = crosshead speed (in/min)

CHS = chart speed (in/min)

l_c = final length of crack (in)

w_c = crack width (in)

VI. RESULTS AND DISCUSSION

The fracture surface work of a material is the amount of energy required to create a fractured surface. Values measured by the double cantilever beam test for the Kerimid 601 specimens are presented in Table 3. The low value of the unmodified Kerimid 601 is common to other crosslinked resins such as ERLA 4617 and styrene cured polyesters (10,21), all of which are in the range of 0.20 in-lbs/in².

The brittle nature of Kerimid 601 was observed in fracture surface micrographs in the load-displacement curves, and in compression tests. These results will be compared to piperidine cured Epon 828, a system that has been shown to be toughened by a rubber particle phase (22), from its unmodified γ value of 0.6 in lbs/in².

The load displacement curves from the DCB tests of Kerimid 601 and Epon 828 are presented in Figure 7. A typical stick-slip record was observed for Epon 828, which suggests that some energy absorbing mechanism is active before crack initiation. Streaks of tufted material perpendicular to the crack initiation site, indicative of plastic flow, support this idea: Figure 8. In contrast, a continuous mode of crack propagation is observed for Kerimid 601 and no sign of plastic flow at crack initiation is seen in Figure 9. Compression test behavior, shown in Figure 10, confirms the ability of Epon 828 to deform plastically while Keramid 601 undergoes very little yielding. These comparisons suggest that the molecular mobility of Kerimid 601 is much less than that of the Epon 828. This is consistent with the modest increase in

toughness of the silicone rubber modified Kerimid 601, Table 2, and the high incidence of secondary cracks which originate from the rubber particles on the fracture surface, Figure 11.

An alternative to rubber particle toughening is a chemical blend of the elastomer with the resin. This was attempted by adding 5% Hycar ATBN to the Kerimid 601 by the procedure discussed in the sample preparation section. It was hoped that ATBN would react with the bismaleimide in the same manner as the aromatic diamine, increasing its ability to withstand extreme processing conditions. Unfortunately, the heterogeneity from mixing and curing produced a sample whose crack deviated from the slotted plane when tested. (This heterogeneity can be observed in the fracture surface, Figure 12, the smooth region being free of ATBN, whereas the coarse region contains it.) A valid toughness value could not be determined but the load-displacement curve of the ATBN modified specimen, Figure 13, suggests some toughening did occur.

Another analytical technique which was informative was infrared spectroscopy. This was used to detect ATBN in the Kerimid 601 specimen and to determine if the polyimide polymerization had been altered in any way. First, the polymerization of pure Keramid 601 was monitored. IR spectra, obtained by forming the Keramid prepolymer powder, and the powder from the resulting polyimide into KBr pellets (22) are shown in Figures 14 and 15. Using Figure 3 for reference, the peaks in these spectra can be assigned to various chemical species. As expected, the primary aromatic amine peaks at 3460 cm^{-1} , 3360 cm^{-1} , 1620 cm^{-1} , and 1280 cm^{-1} in the prepolymer, are replaced by a fairly broad

secondary aromatic amine peak at 3475 cm^{-1} in the polyimide. Some residual primary amine bonds indicate that not all of the aromatic amines have reacted with the bismaleimide. The other major chemical species expected to disappear upon polymerization are the double bonds in the bismaleimide. These peaks are located at 3100 cm^{-1} , 3040 cm^{-1} , 2900 cm^{-1} , 2840 cm^{-1} , 1400 cm^{-1} , 960 cm^{-1} , 820 cm^{-1} and 700 cm^{-1} . It can be seen from the spectra that the reaction of the double bonds also is not complete. The one peak that does retain its intensity after polymerization is at 1700 cm^{-1} , and is attributed to the carbonyl groups in the bismaleimide. The peaks that correspond to the aromatic groups and the imide bonds appear at 1780 cm^{-1} , 1520 cm^{-1} , 1380 cm^{-1} , and 1180 cm^{-1} .

A spectrum of the ATBN, obtained by placing a few drops of the liquid rubber between two NaCl plates, appears in Figure 16. The peaks at 2940 cm^{-1} , 2850 cm^{-1} , 1450 cm^{-1} , 970 cm^{-1} , and 920 cm^{-1} are assigned to the butadiene component, those at 2250 cm^{-1} and 1450 cm^{-1} are due to the acrylonitrile, and the broad peak at 3450 cm^{-1} corresponds to the secondary amine groups. The carbonyl peak at 1700 cm^{-1} is an artifact of the ATBN synthesis.

When the Kerimid 601 was modified by 5% ATBN, a number of interesting observations derive from the resulting spectrum, Figure 17. The bands in the spectrum that signify the presence of ATBN are located at 2940 cm^{-1} , 2250 cm^{-1} , 1450 cm^{-1} , 1440 cm^{-1} , and 970 cm^{-1} . Most of these peaks are relatively small, but the one at 2940 cm^{-1} is quite strong compared to the unmodified Kerimid 601, Figure 18. Another important observation is that the spectrum

in Figure 16 is not the stoichiometric sum of its parts. For example, the peak at 970 cm^{-1} is approximately half the intensity of the one at 2940 cm^{-1} , whereas they have the same intensity in the ATBN spectrum, Figure 17. The 2940 cm^{-1} band is also common to alkane groups, but the 940 cm^{-1} peak corresponds only to double bonds. Thus, the ATBN may have been cured, and the 2940 cm^{-1} peak would correspond to the formation of alkane groups. The decrease in intensity of the peak at 1620 cm^{-1} with respect to the unmodified Kerimid 601 indicates the aromatic amine may have also cured the ATBN.

Kerimid 601 was also modified with Teflon, giving the results in Table 3. As discussed earlier, the basic mechanism of toughening depends on the mechanical behavior of the Teflon. The only influence which the polyimide might have is its ability to wet the fibers. If the wetting is good, fiber drawing would be preferred to pullout during fracture and, by improving the efficiency of drawing, a greater toughness can be achieved. The micrograph in Figure 19 shows Teflon covered with a few droplets of Kerimid 601 which do not appear to wet well.

Three different processing techniques were employed to fibrillate the Teflon granules, Table 2. The specimens which had been blended in Epon 828, Class B, did not show large increases over the control. Better results come from the specimens containing the milled or injection molded Teflon. The milled Teflon was obtained in two Lots: specimens prepared from Lot 1 exhibited a slightly greater fracture toughness than those prepared from Lot 2. In both cases, a decrease was observed when the Teflon also was blended in Epon 828. The purpose of the blending was

to fibrillate the Teflon sheet more, increasing the dispersion of it in the specimen. The adverse effect may be due to ineffective washing and incomplete removal of the Epon 828.

A micrograph of the milled material, Figure 20, shows little fibrillation. The Teflon forms small sheets which are evident in the fractographs, Figures 21 and 22, where their deformation probably contributes a major component of the total crack resistance.

The injection molded material was the most effective: an eightfold increase in the fracture surface work over that of unmodified Kerimid 601 was observed for a specimen containing 5% Teflon. Figure 23 shows the extensive fibrillation produced in this way while Figure 24 illustrates the difficulty of dispersing the fibers in the Kerimid 601. In Figure 25, the great mechanical drawing undergone by the fibers during fracture is evident and the force-displacement curve, Figure 26, shows the fibers bridge the crack in the matrix, restraining its forward advance until they are pulled apart. Even better prior fibrillation of the Teflon, better dispersion of it in the matrix, and higher volume fractions can probably achieve a 20-30 fold increase in fracture toughness.

VII CONCLUSIONS

Kerimid 601 is a brittle polymer with the same fracture surface work value as some high temperature epoxies and styrene cured polyesters. These are not toughened much by a dispersed rubber phase; the same appears to be true of the Kerimid 601. Perhaps by

chemically modifying the resin with ATBN, a toughened polymer can be obtained and this will be explored more fully.

Teflon microfiber toughening is based upon the mechanical behavior of the fibers, though wetting may play an important role. As much as an eightfold increase in toughness was observed in specimens with 5% Teflon which had first been fibrillated by undergoing injection molding in P.M.M.A. Better dispersion of a higher volume fraction of such fibers should produce an even greater toughening effect. Work toward such is continuing.

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TABLE 1

Properties of Hycar ATBN (1300X16)

Viscosity, Brookfield, mPa s or cP at 27° C (81°)	225,000
Total equivalent weight	800 - 1000
Acrylonitrile , %	16.5
Specific gravity at 25° C (77°)	0.956

Table 2

Preparation Techniques - All start with Teflon as received from Du Pont.

<u>Designation</u>	<u>Preparation</u>
Class A	None. Control material.
Class B	<ol style="list-style-type: none"> 1) Blend 10 parts Teflon to 100 parts Epoxy 828 in Waring Blender for 15 minutes. 2) Wash thoroughly with acetone to remove Epoxy 828
Class C	<ol style="list-style-type: none"> 1) Place Teflon in rubber mill for 15 minutes. 2) Break up sheet in Waring blender, using methanol as mixing medium Extra step used for some of the Teflon: <ol style="list-style-type: none"> 1) Blend 10 parts Teflon obtained from step 1 in 100 pts Epoxy 828 for 60 minutes at 5 minute intervals 2) Wash thoroughly with acetone to remove Epoxy 828
Class D	<ol style="list-style-type: none"> 1) Injection mold 5 parts Teflon in 100 parts PMMA 2) Crush up extrudate and repeat molding cycle. 3) Wash thoroughly with acetone to remove PMMA. 4) Break up resulting Teflon strands in Waring blender, using methanol as a mixing medium.

Table 3

Fracture surface work values for Keramid 601 specimens

<u>Modification</u>	$\gamma \left(\frac{\text{in-lb}}{\text{in}^2} \right)$
Unmodified Resin	.20
5% Silicone rubber	.25
5% ATBN (1300x16)	Invalid Tests
Class A-20% Teflon	.24
Class B-20% Teflon	.54
Class C- Teflon	
Lot 1 -	
not treated with Epoxy 828	
-5% Teflon	.76
-10% Teflon	.92
treated with Epoxy 828	
-5% Teflon	.34
-10% Teflon	.54
Lot 2	
not treated with Epoxy 828	
-10% Teflon	.70
treated with Epoxy 828	
-5% Teflon	.44
Class D - 5% Teflon	1.57

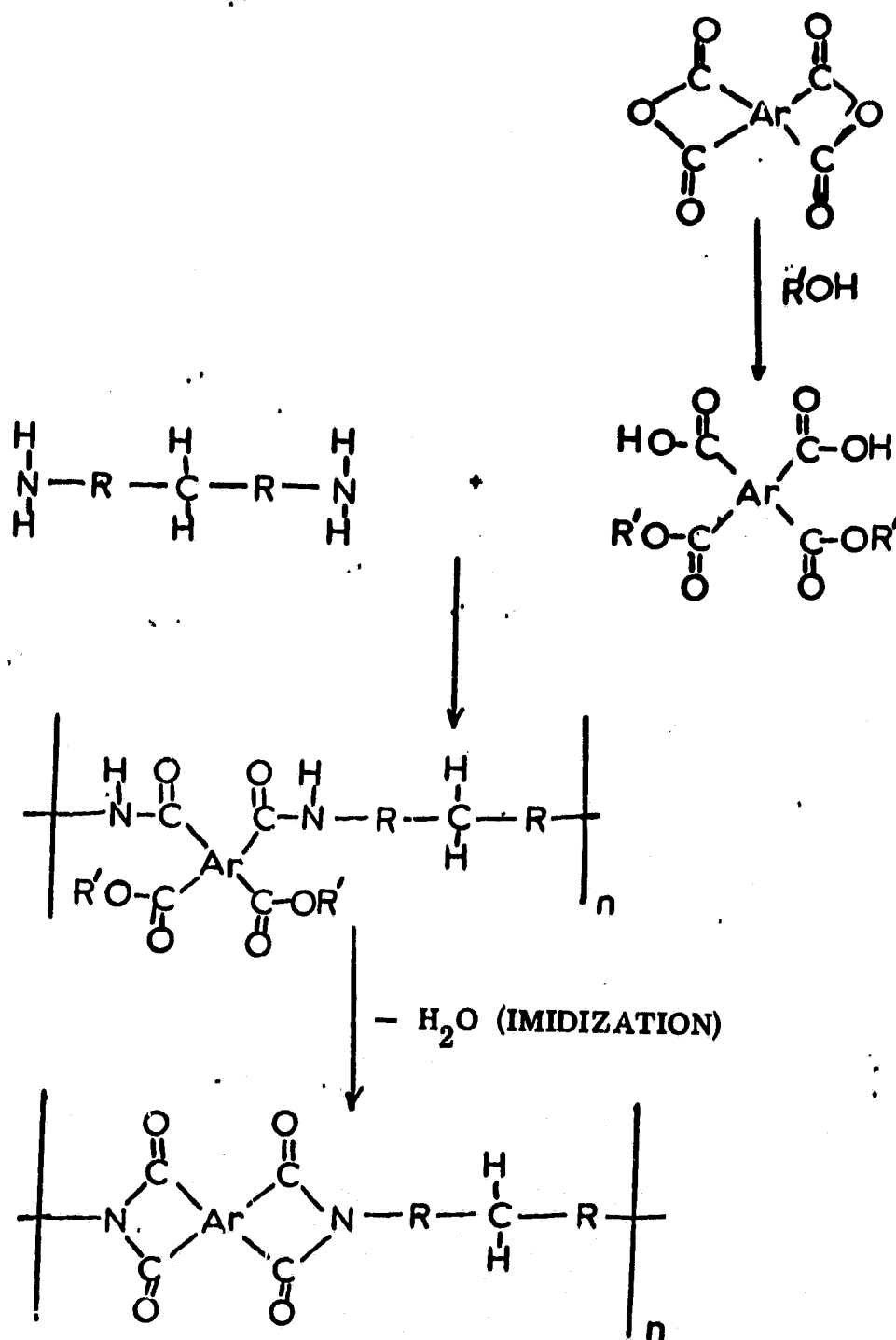


FIGURE 1.
POLYIMIDE REACTION OF CONDENSATION TYPE PREPOLYMER.

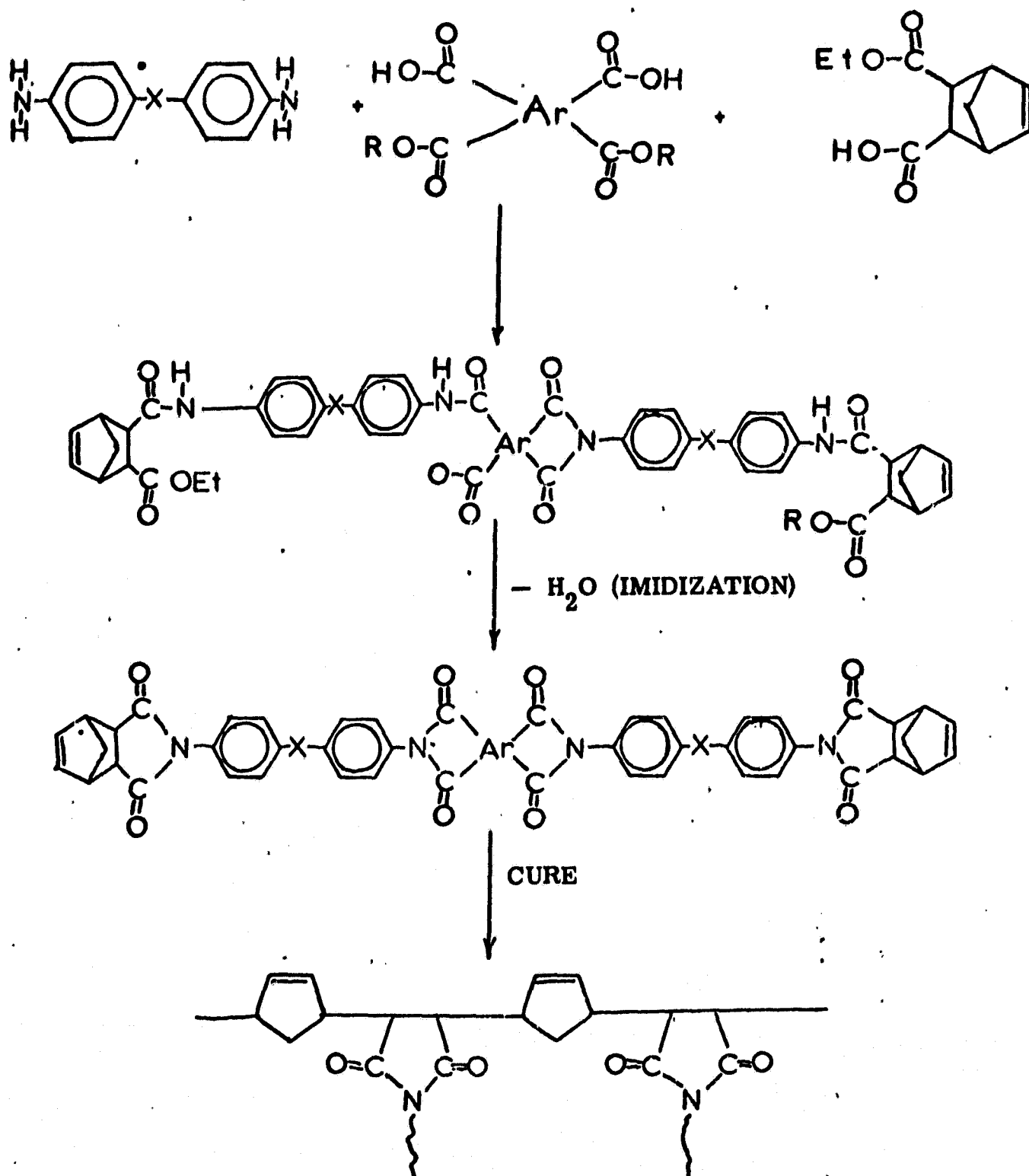
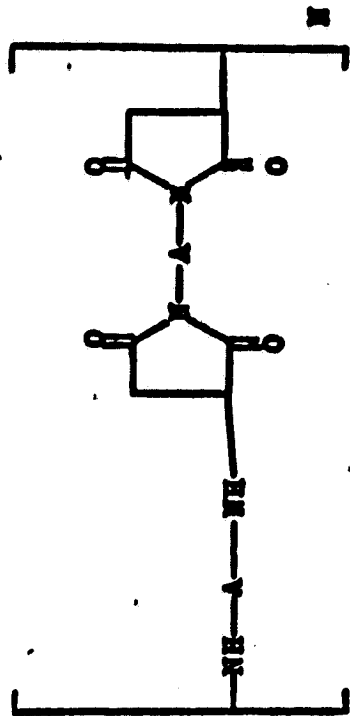
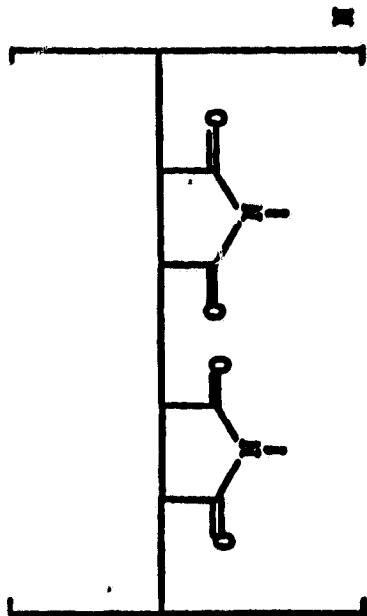
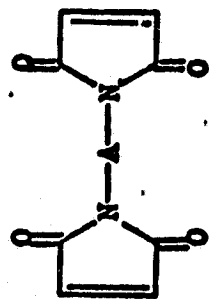


FIGURE 2.
POLYIMIDE REACTION OF ADDITION TYPE PREPOLYMER.



A- Aromatic

FIGURE 3.
KERIMID 601 CHEMISTRY.

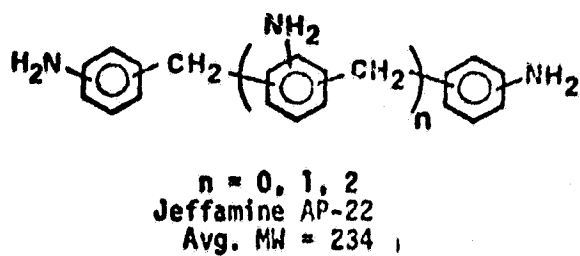
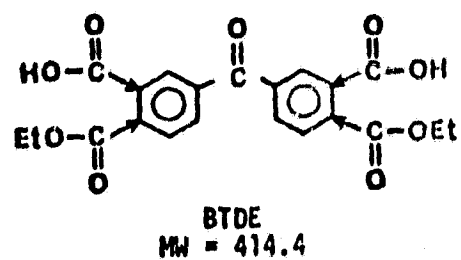
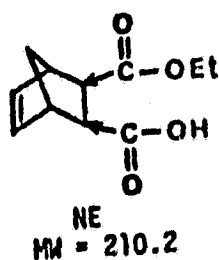


FIGURE 4.
CHEMICAL CONSTITUENTS OF LARC 160.



FIGURE 5.
SILICONE RUBBER PARTICLES (275 X).

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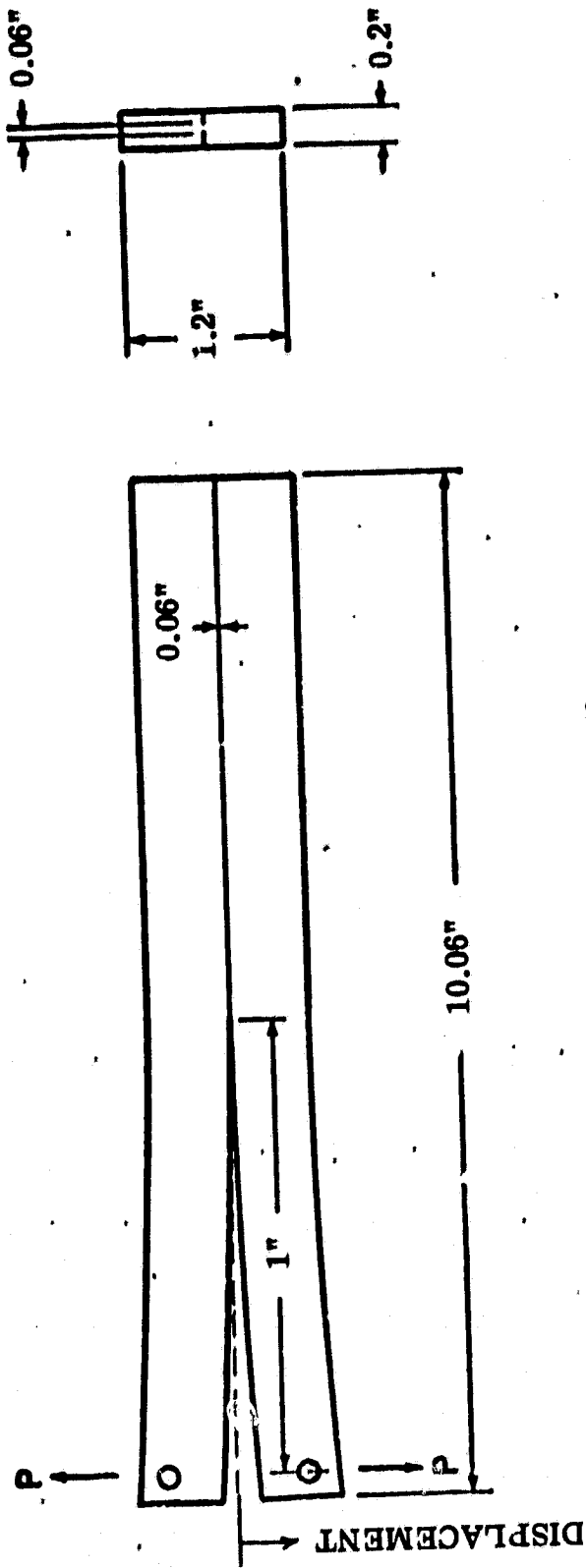


FIGURE 6.
DOUBLE CANTILEVER BEAM SPECIMEN.

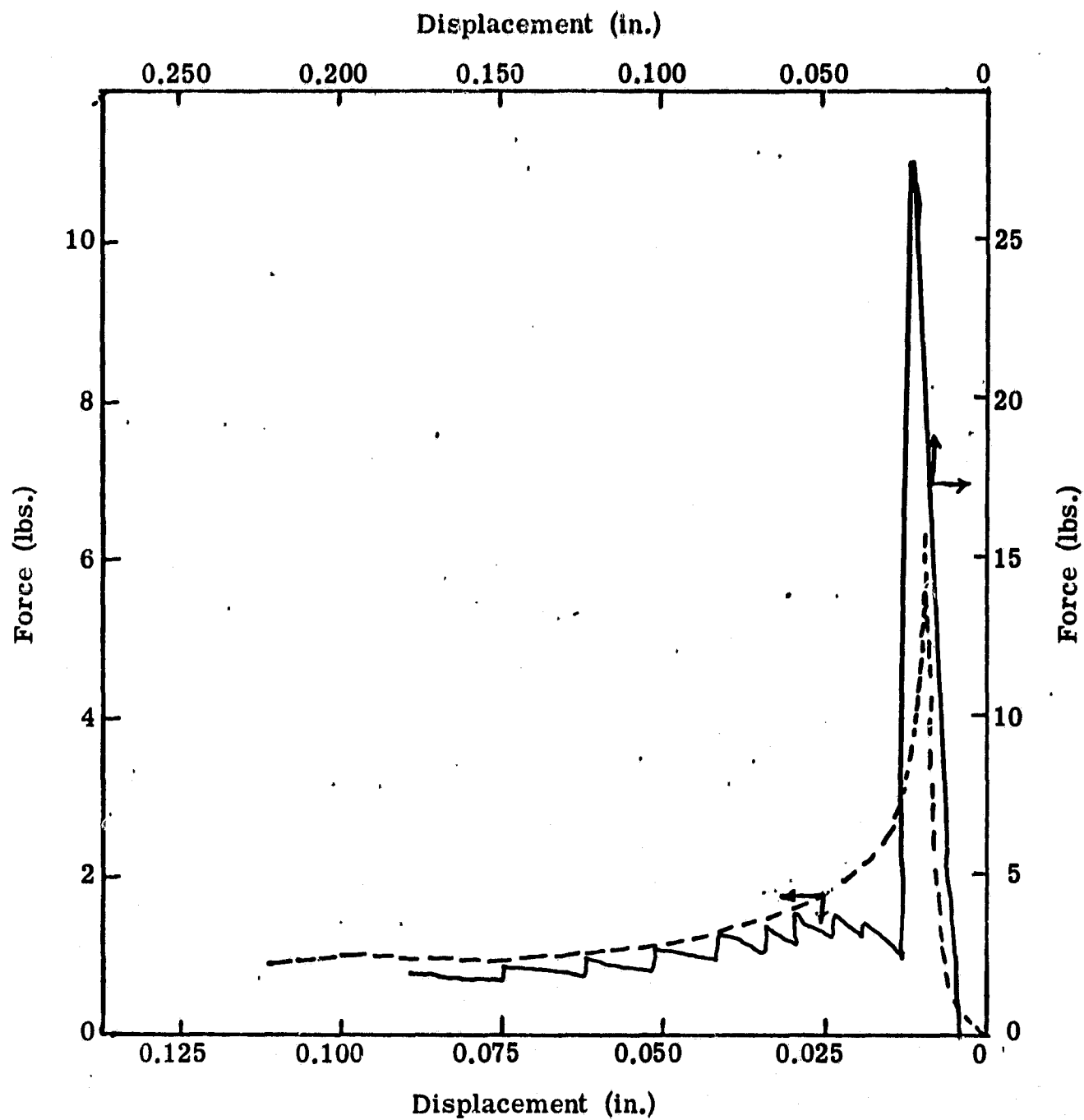


FIGURE 7.
FORCE-DISPLACEMENT CURVES FOR EPON 828 (—)
AND KERIMID 601 (---).

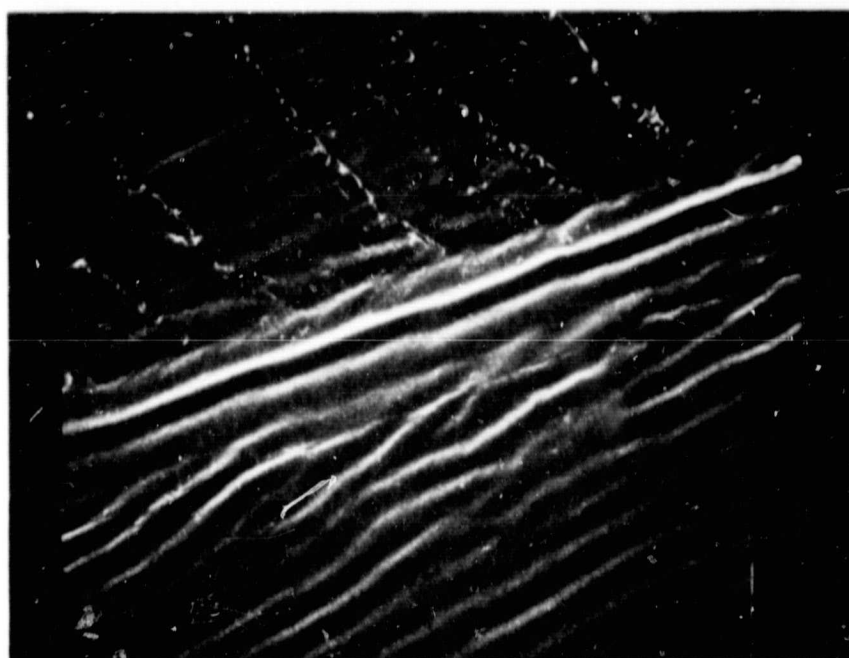


FIGURE 8.

DCB FRACTURE SURFACE OF UNMODIFIED EPON 828
CURED WITH 5% PIPERIDINE (540 X).

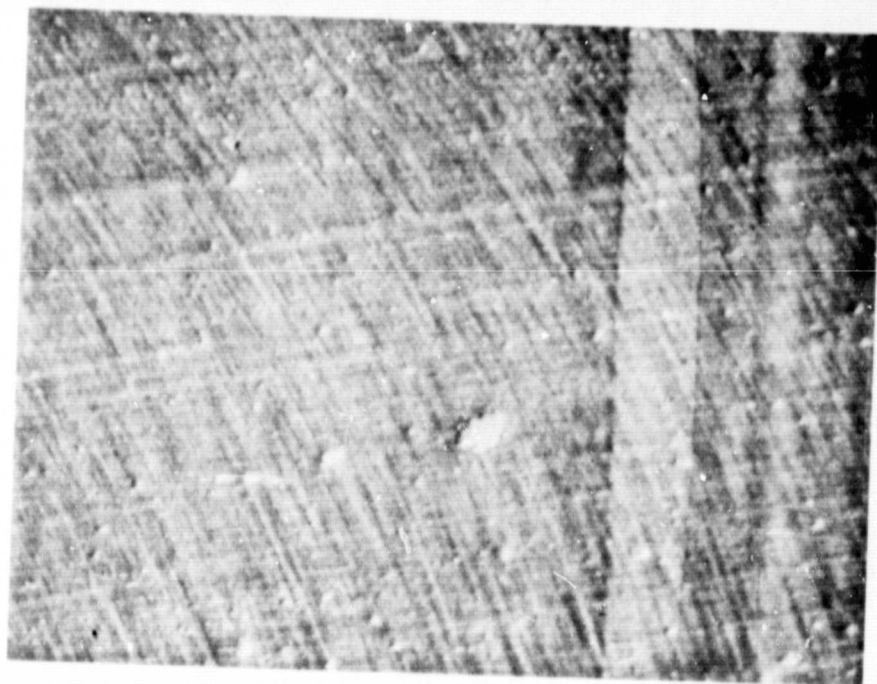


FIGURE 9.
DCB FRACTURE SURFACE OF KERIMID 601 (1000 X).

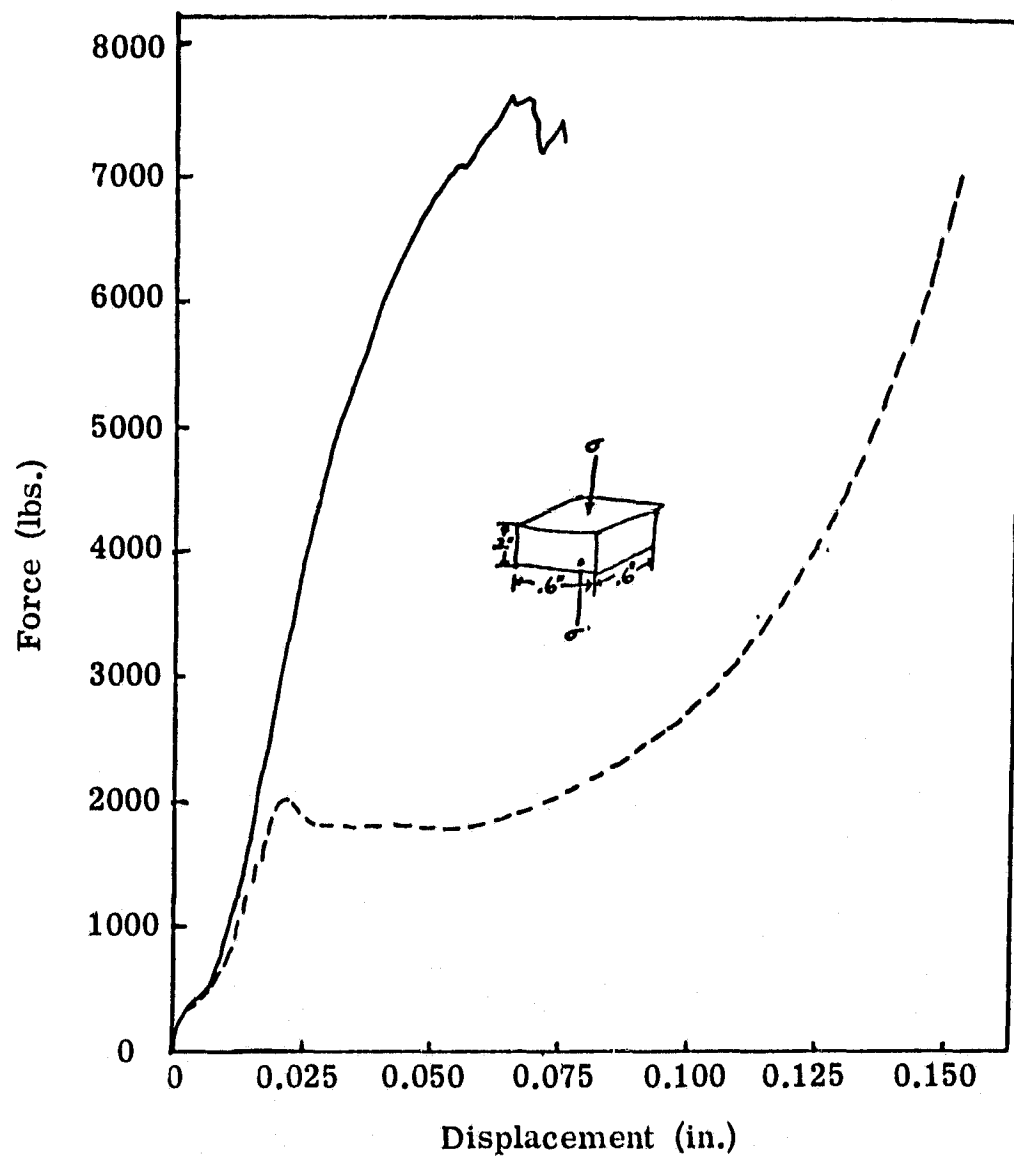


FIGURE 10.
COMPRESSION TEST FOR EPON 828 (---)
AND KERIMID 601 (—).

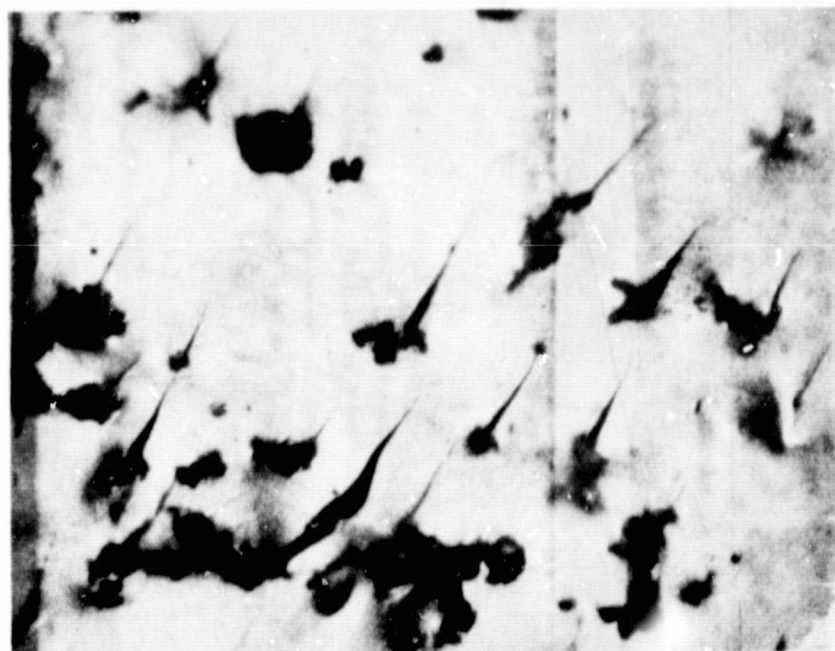


FIGURE 11.
DCB FRACTURE SURFACE OF 5% SILICONE RUBBER-
MODIFIED KERIMID 601 (345 X).

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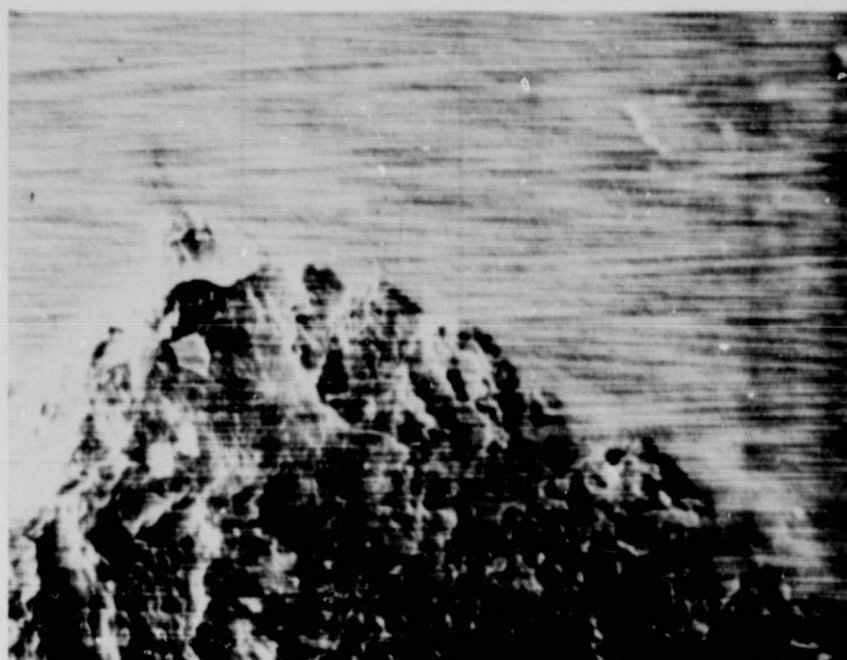


FIGURE 12.

DCB FRACTURE SURFACE OF 5% ATBN-MODIFIED
KERIMID 601 (1000 X).

Rough region is rubber particle.

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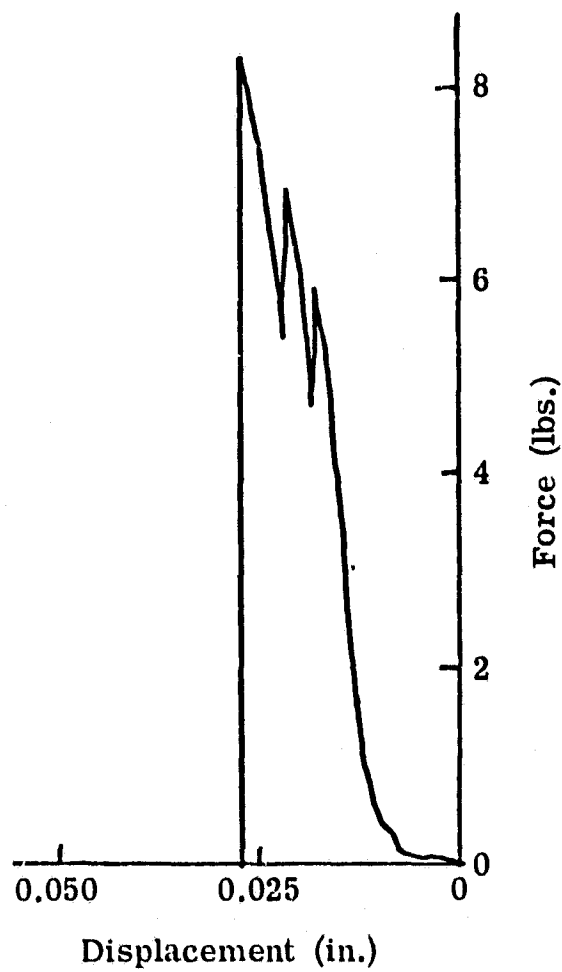


FIGURE 13.
FORCE-DISPLACEMENT CURVE FOR 5% ATBN-
MODIFIED KERIMID 601.

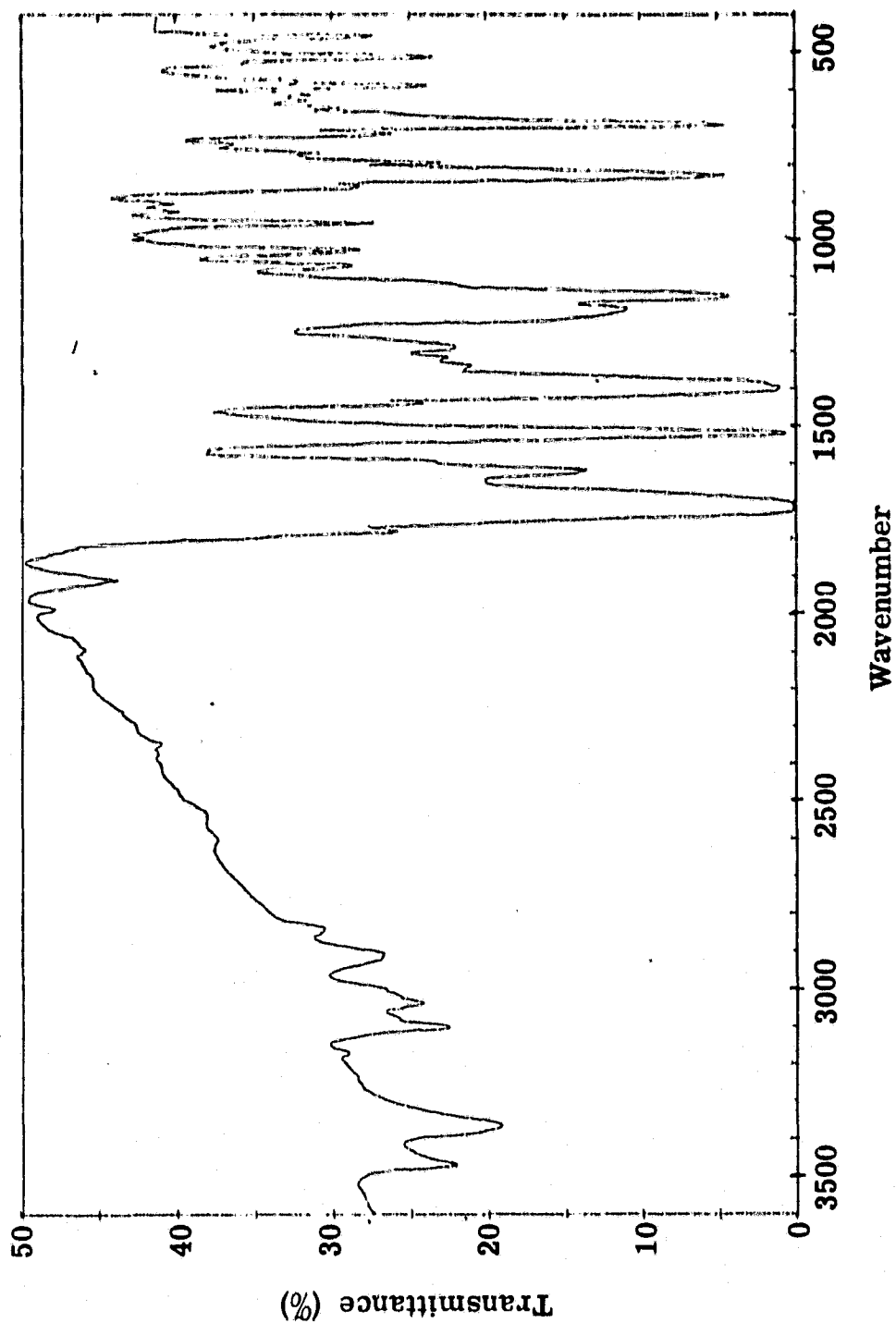


FIGURE 14.
FTIR SPECTRUM FOR KERIMID 601 PREPOLYMER,
FROM KBr PELLET.

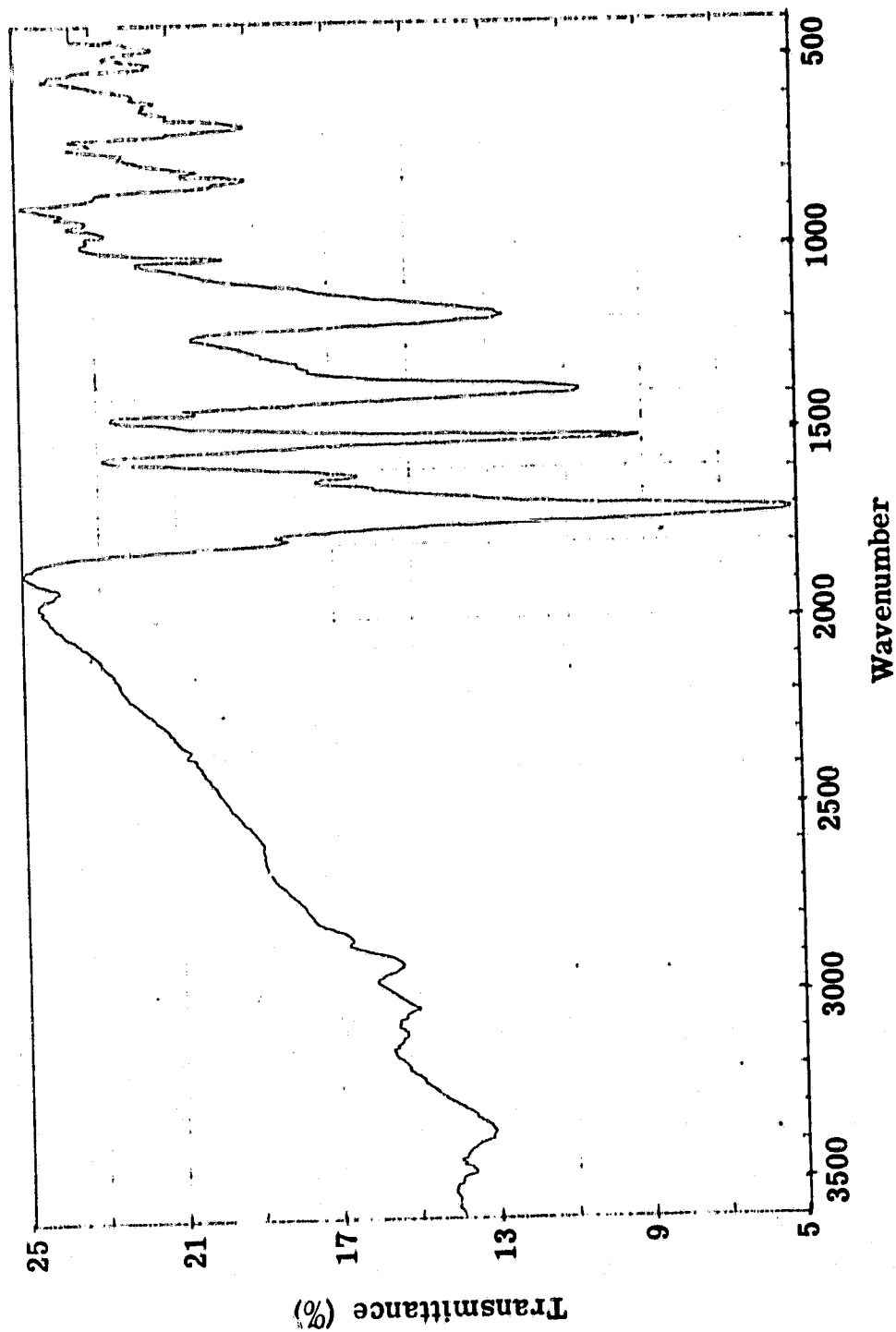


FIGURE 15.
FTIR SPECTRUM FOR KERAMID 601, FROM KBr PELLET.

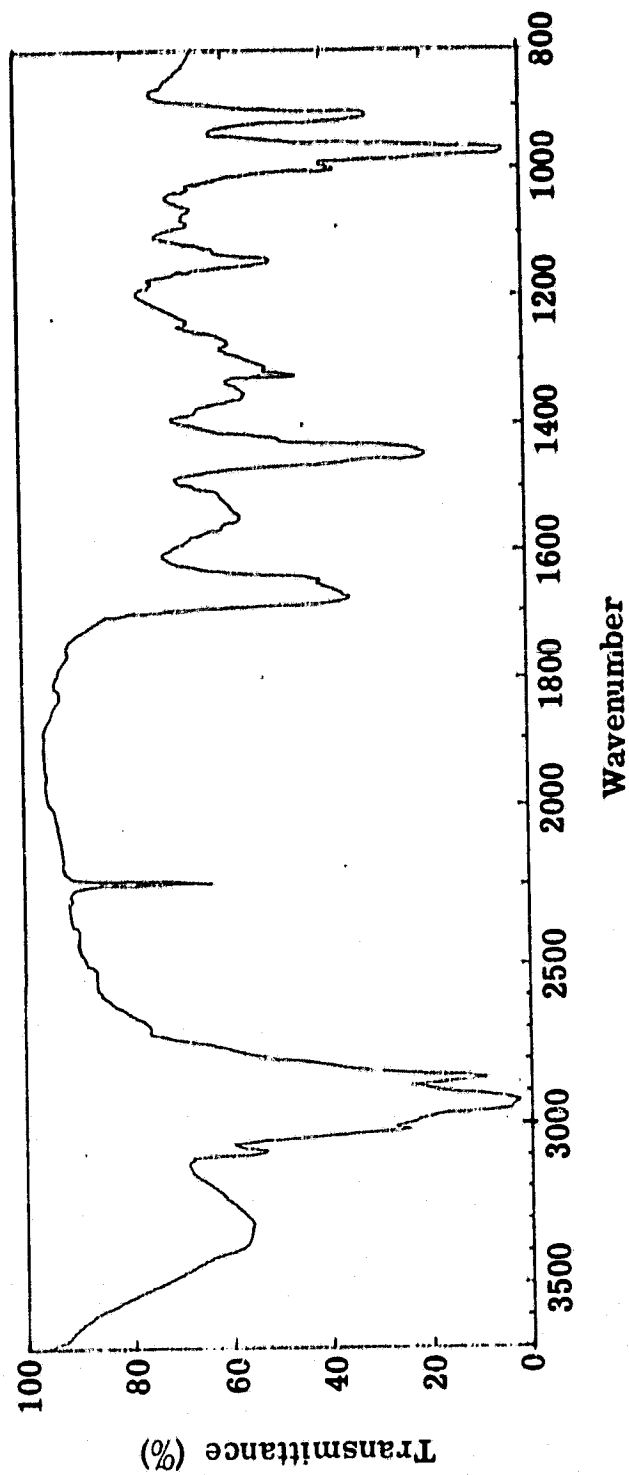


FIGURE 16.

IR SPECTRUM OF Hycar ATBN (1300x16).

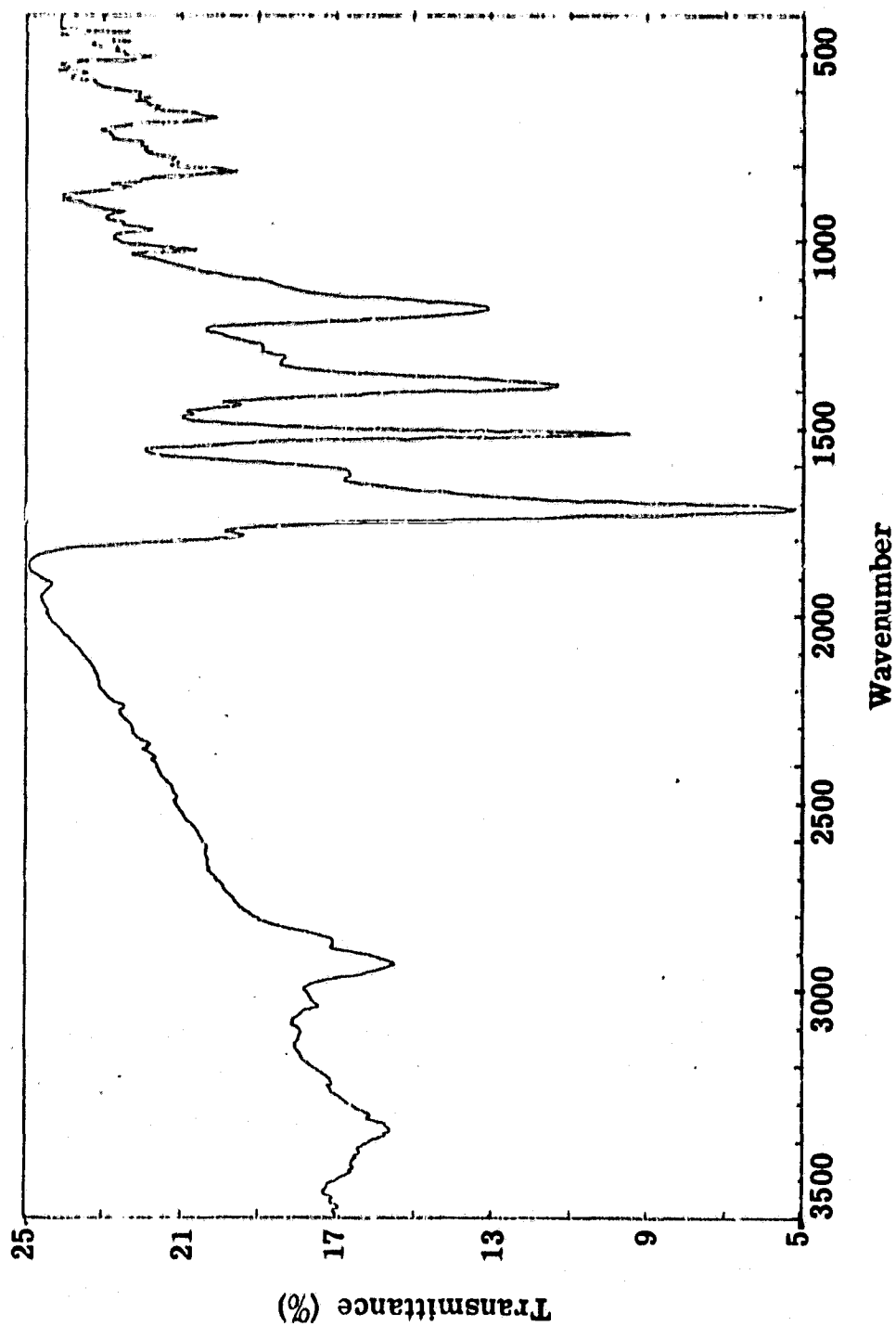


FIGURE 17.

FTIR SPECTRUM FOR 5% ATBN-MODIFIED KERAMID 601,
FROM KBr PELLET.

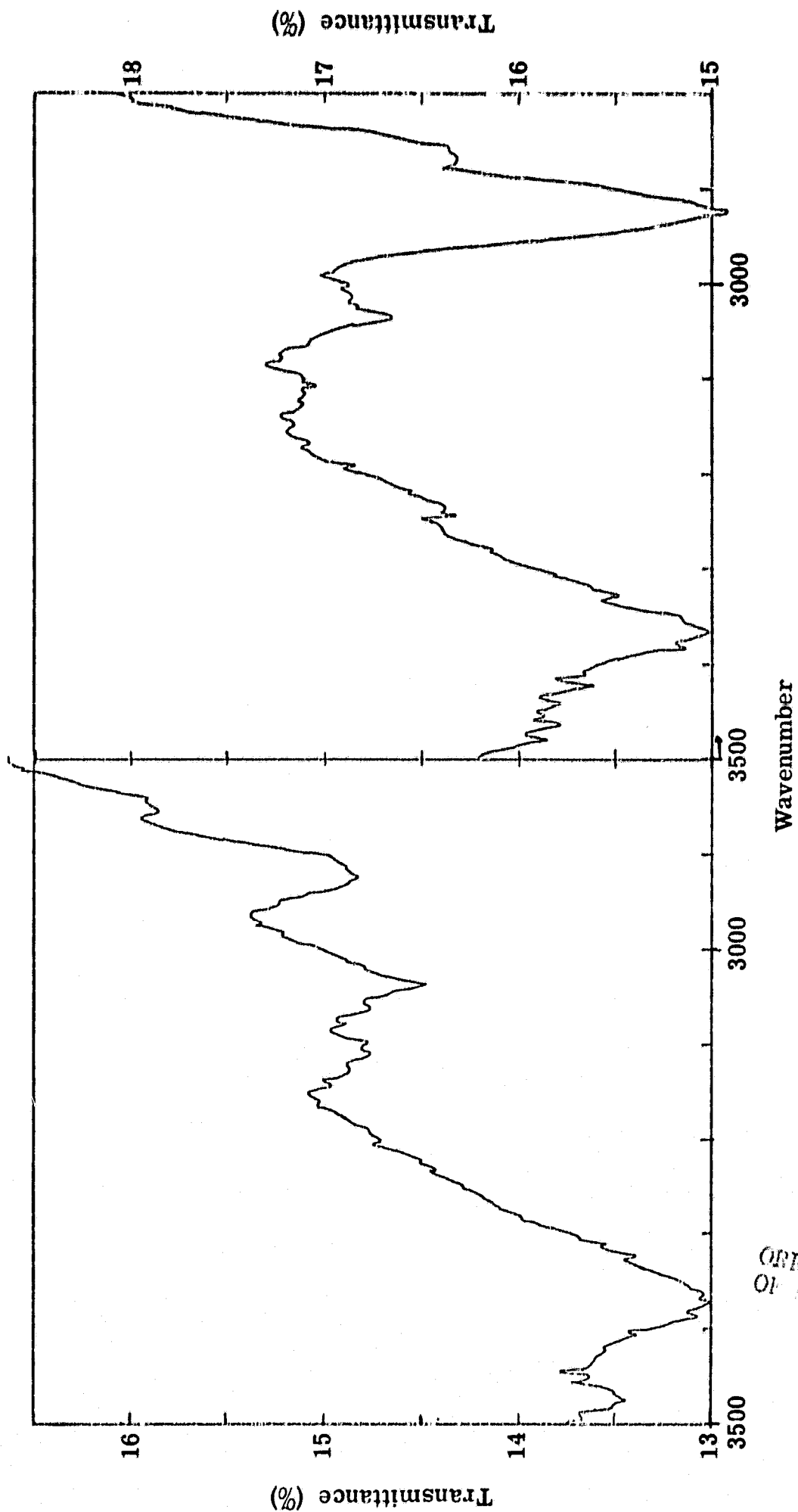


FIGURE 18.
ENLARGED FTIR SPECTRUM OF KERIMID 601 (LEFT)
AND 5% ATBN-MODIFIED KERIMID 601 (RIGHT).

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FIGURE 19.
PARTICLE OF TEFLON COVERED WITH DROPLETS
OF KERIMID 601 (500 X).

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FIGURE 20.
MILLED TEFLON (1000 X).

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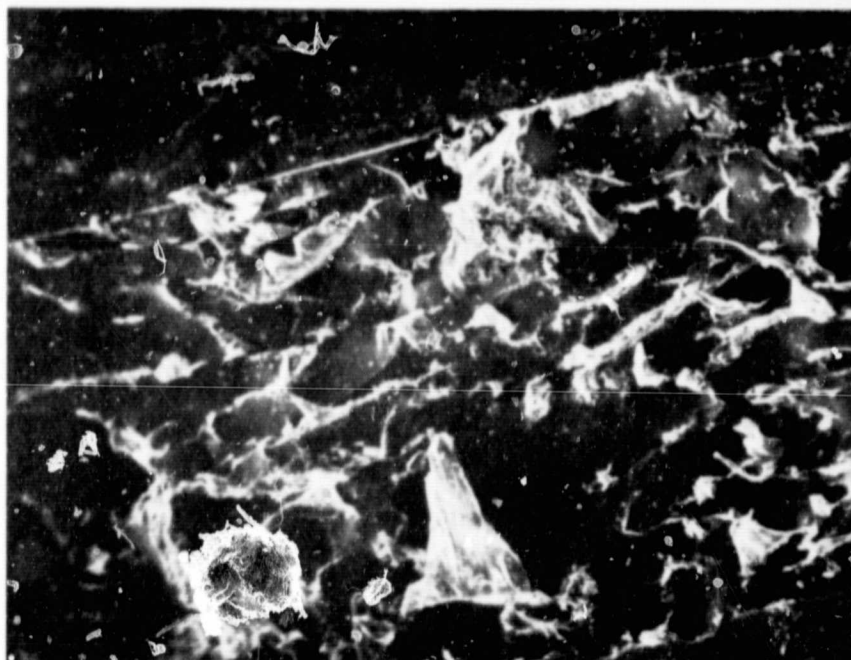


FIGURE 21.

DCB FRACTURE SURFACE OF KERIMID 601
MODIFIED BY 5% MILLED TEFLON (30 X).



FIGURE 22.
ENLARGEMENT OF REGION IN FIGURE 21 (300 X).

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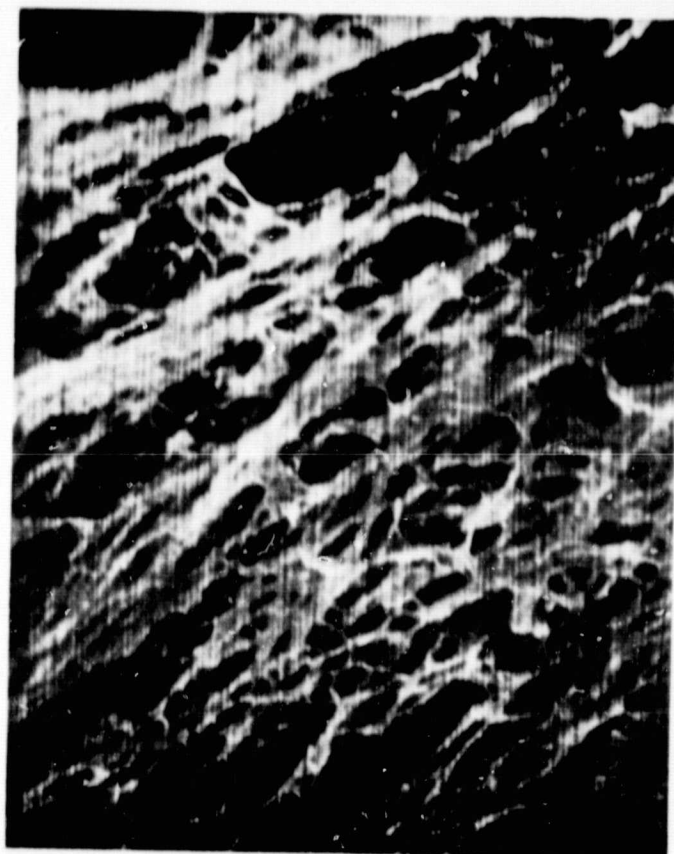


FIGURE 23.
INJECTION MOLDED TEFLON (3000 X).



FIGURE 24.

DCB FRACTURE SURFACE OF KERIMID 601 MODIFIED
BY 5% INJECTION MOLDED TEFLON (30 X).

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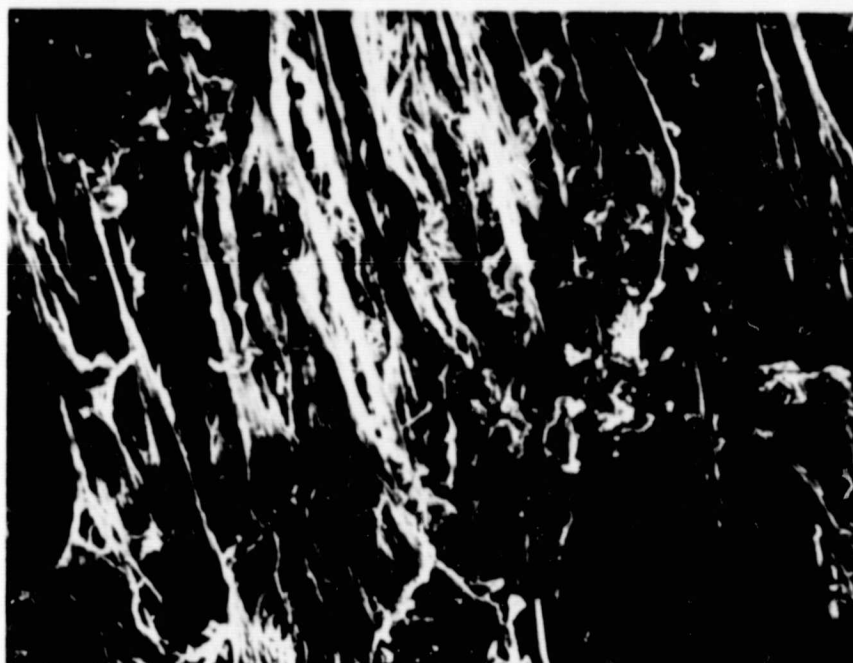


FIGURE 25.
ENLARGEMENT OF TEFLON-RICH REGION
IN FIGURE 24 (300 X).

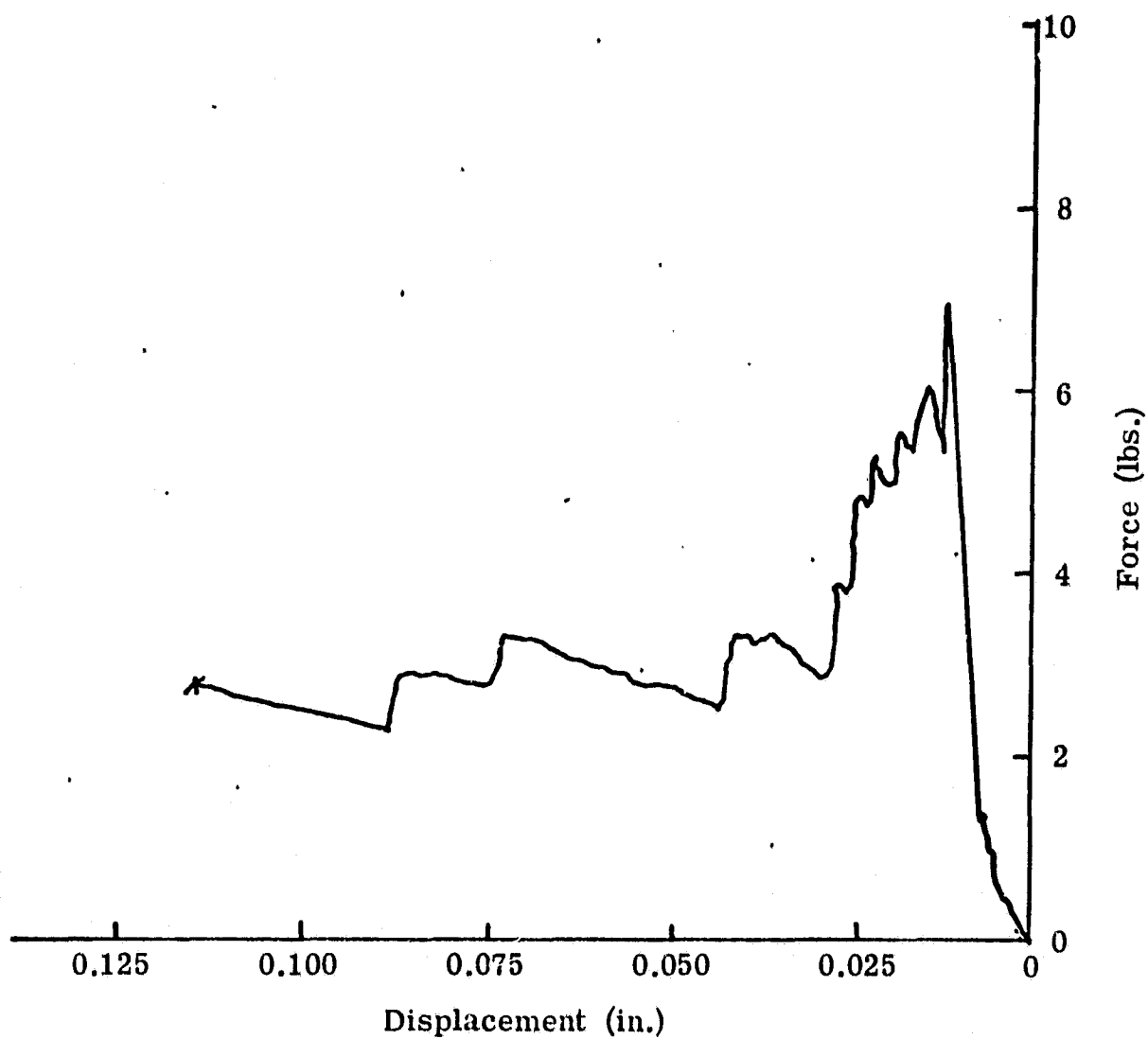


FIGURE 26.
FORCE-DISPLACEMENT CURVE FOR 5% TEFLON-
MODIFIED KERIMID 601.